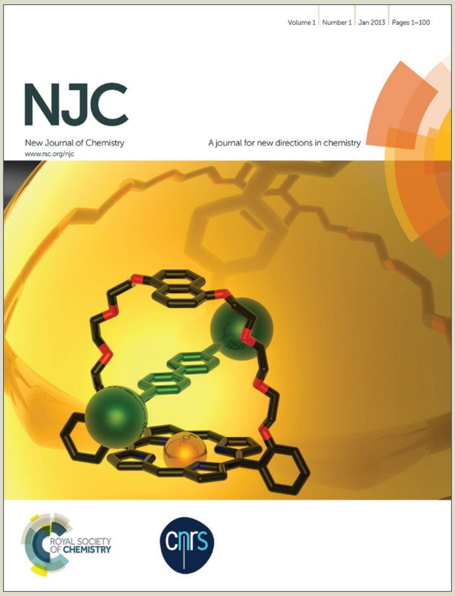

Journal Name

ARTICLE

Copolymers from norbornene and norbornadiene with organized morphologies and high T_g values obtained via ROMP with highly reactive [RuCl$_3$(PCy$_3$)$_2$] complex

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The [(RuCl$_3$(PCy$_3$)$_2$] complex presented high reactivity for Ring Opening Metathesis Polymerization (ROMP) of norbornadiene (NBD) in non-degassed solution upon addition of ethyl diazoacetate (EDA). Quantitative yields of polyNBD were obtained instantaneously at 25 °C. ROMP of norbornene (NBE) better occurred at 50 °C for 60 min, with 95% of isolated polyNBE. Copolymers with different porous structures were obtained from ROMP of NBE in the presence of NBD with different starting [NBE]/[NBD] molar ratios at 25 °C. SEM micrographs showed a more organized porous structure as the NBD loading decreased. A well-defined honeycomb-like pattern for the copolymer from the run with NBE:NBD molar ratio load of 5000:500 was recorded. The T$_g$ values varied from 37 °C in polyNBE to 90 °C in poly[NBE-*co*-NBD] as the NBD loading increased.

Introduction

Ring Opening Metathesis Polymerization (ROMP) of cyclic olefin has been employed to prepare polymers with different sizes and structures, with diverse pendant groups along the chains or different types of copolymers.[1-8] These features follow the tendency in polymer chemistry to obtain macromolecules with controlled structure and morphology.[2-4, 9, 10]

ROMP is catalyzed by a transition metal-carbene complex (L$_n$M=CHR) through a metallocyclobutane intermediate produced from an intermolecular interaction between the metal-carbene moiety and the olefin, as illustrated in Scheme 1.[6, 11, 12] The orbital coplanarity in {olefin-M=CHR} moiety is critical to the success of this reaction. The ancillary ligands (L) in the complex can influence the occurrence and rate of this step by allowing the correct coordination of the olefin in a geometric arrangement to enable orbital overlap with the metal-carbene moiety.[6, 11-13] Usually, ancillary ligands in ROMP are bulky and good σ-donors.[6, 11, 12] Consequently, the active species presents elevated electron density and variable coordination number which provide an efficient catalytic reaction. Because of these electronic and steric requirements, the complexes are usually sensitive to molecular oxygen and the reactions must be performed under air-free atmosphere.

[RuCl$_2$(=CHPh)(PCy$_3$)$_2$] polymerized 100 equivalents of norbornene within seconds, but PDIs are much broader (2.0-2.5) than with [RuCl$_2$(=CHPh)(PPh$_3$)$_2$], supposedly due to backbiting and chain transfer as side reactions.[14] Benzylidene complexes such as [RuCl$_2$(=CH-*p*-C$_6$H$_4$X)(PCy$_3$)$_2$] (X =H; NMe$_2$; OMe; Me; F; Cl; NO$_2$) are extremely active ROMP catalysts compared with their PPh$_3$ analogous, and have been shown to induce living polymerization of functionalized norbornenes and 7-oxanorbornenes in solution.[14-16] ROMP of highly strained monomers including functionalized norbornenes, 7-oxanorbornenes, and variously substituted cyclobutenes proved to be polymers with exceptionally narrow molecular weight distributions (PDIs< 1.1).[14-16]

Porous poly(norbornene) is a soaking material for oil spills because of its porous structure. Porous polymers are of interest for applications in microelectronics, biomedical devices, membrane processes, and to synthesize porous ceramics or porous carbon.[17-19] Besides remarkable features resulting from ROMP reactions, polymers with addressed morphologies and T_g values can be obtained. The honeycomb films exhibit a hexagonal array of micrometric pores and have received considerable interest owing to the simple, inexpensive, and robust mechanism of pattern formation, such as large space area, good structural stability, and high mechanical strength.[20] A large range of polymers from ROMP has been used to target different surface properties, e.g., iridescence, photoluminescence, cell adhesion, bio-molecule recognition, intrinsic properties of hybrid films, stimuli-responsive

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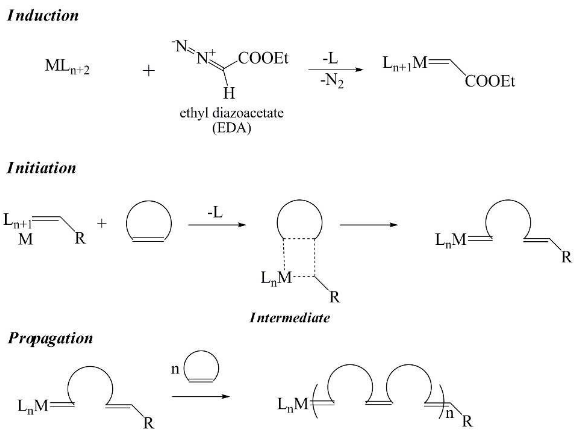
structured surfaces, and super hydrophobic character of surfaces derived from honeycomb films.[21-23]



Scheme 1. Illustration of ROMP catalyzed by a metal-carbene species.

Over the past years, our research group has made a considerable effort to tune ancillary ligands in $[RuCl_2(PR_3)_y(amine)_x]$ complexes in search of alternative catalysts for ROMP.[24-31] Our motivation is to develop compounds that are non-sensitive to air, moisture, light and warmth; that can be easily stored; and that can match large practical applications in the presence of molecular oxygen from air atmosphere.[32] The metal-carbene moiety has been generated *in situ* from reaction with diazo compounds, contrary to the cases with pre-synthesized metal carbene complexes such as the benzylidene-type complexes. Of course, an induction period precedes ROMP initiation, and this step must be considered when interpreting the initiation and propagation steps in the ROMP reaction. However, we believe that there is room for the studying of diverse types of starting complexes when analyzing the cost-benefit ratio for a particular application.

In this paper, we report a surprising finding from a one-pot synthesis reaction between $RuCl_3$ and PCy_3, a five-coordinate Ru^{III}-PCy_3 complex (**1**), which polymerized norbornene (NBE) and norbornadiene (NBD) *via* ROMP very fast in non-degassed solutions. The reactions are so exothermic that can burn one's hand when holding the reaction flask. The starting Ru^{III} complex presents low π-electronic density to activate the olefin, enabling the reaction. In the past, we investigated ROMP with $RuCl_3$ and concluded that a Ru^{II} species was generated *in situ*, thus reaching a low spin d^6 electronic configuration to activate the olefin in the reaction.[33, 34] However, the reactions could not occur so fast where coordination of ligands and a redox reaction must occurr before the induction period. In the current case, the reactions have occurred very fast. In contrast, the presence of PCy_3 as ancillary ligand offer the required conditions, as previously mentioned, of a strong σ-donor ($pK_a = 9.7$) to provide high electronic density to the metal center and present a large cone angle ($\theta = 170^o$). This can open an extra generation of non-carbene complex for ROMP. Thus our goal was to explore the activity of this complex for ROMP of NBE and NBD under different conditions of reaction time, temperature, and monomer concentration, followed by copolymerization of NBE with NBD where polymers with non-usual morphological aspects were obtained. Different loads of NBD as cross-linking agent were tested because cross-linked polymers present important advantages over their non-cross-linked analogous, such as superior mechanical and chemical properties, high thermal stability, and low temperature dependence on viscosity.[4, 35-41]

Experimental

General remarks

All the solvents used were HPLC grade and were distilled from the appropriate drying agents immediately prior to use. Other commercially available reagents were used without further purification. $RuCl_3{\cdot}xH_2O$, norbornene (NBE),norbornadiene (NBD), tricyclohexylphosphine (PCy_3) and ethyl diazoacetate (EDA) from Aldrich were used as achieved. The room temperature was 23± 1 °C.

Synthesis of $[RuCl_3(PCy_3)_2]$ (1)

PCy_3 (5.8 mmol; 1.62 g) was added to a solution of $RuCl_3{\cdot}xH_2O$ (0.96 mmol; 0.20 g) in methanol (50 mL) under nitrogen atmosphere. The resulting solution was refluxed for 12 h, under magnetic stirring. A yellow precipitate was filtered, washed with warm methanol and dried in a vacuum. Yield: 89%. Elemental Analysis for $RuCl_3C_{36}H_{66}P_2$ calculated C, 56.28; H, 8.66%.;

experimental C, 56.17; H, 8.62%. FT-IR in CsI: υ(C-H) 2935 and 2846, δ(C-H) 1446, υ(C-C) 1002, υ(P-C) 736, δ(C-C) 510, δ(C-C) 490, υ(Ru-Cl) 302 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm) = 46.2 (s).

Synthesis of homopolymer

In a typical ROMP experiment, NBE or NBD was dissolved in non-degassed 2 mL of $CHCl_3$. 1.1 μmol of **1** was added to the reaction solution, followed by EDA. The reaction mixture was stirred for different periods at 25 or 50 °C in a silicone oil bath. At room temperature, methanol (*ca.* 5 mL) was added and the polymer was filtered, washed with methanol and dried in a vacuum before being weighed. The reported yields are average values from catalytic runs performed at least three times.

Syntheses of copolymers from different $[NBE]_{5000}[NBD]_n$load

In a typical ROMP experiment, an NBE amount was dissolved in non-degassed 2 mL of $CHCl_3$ at room temperature to result in a [NBE]/[Ru] = 5000 (it means, $[NBE]_{5000}$). Then NBD was added to result in a [NBD]/[Ru] = n (it means, $[NBD]_n$):for n = 500; 1,500; 3,000. The polymerization reaction was initiated by adding 1.1 μmol of **1**, followed by the addition of 5 μL of EDA ([EDA]/[Ru] = 48). After 180 min, methanol (*ca.* 5 mL) was added and the precipitated material was filtered, washed with methanol, and dried in a vacuum oven at 27 °C until a constant weight was achieved. The reported yields are average values from catalytic runs performed at least three times.

Equipment

Elemental analysis was conducted using a Perkin-Elmer CHN 2400. FTIR spectrum in CsI pellet was recorded using a Bomem FTIR MB 102. Electronic spectra were recorded using a Varian Cary 5G spectrophotometer, using 1 cm path length quartz cells. $^{31}P\{^1H\}$ NMR spectra were recorded using a Bruker AC-200 spectrometer and obtained in $CDCl_3$.

The samples for EPR (Electron Paramagnetic Resonance) were prepared using a quartz tube and the EPR spectra were obtained using an EPR spectrometer Bruker EMX plus. The EPR parameter were: microwave power 2mW, sweep width 2000 Gauss, modulation frequency 100 kHz, modulation amplitude 4 Gauss and 8 scans. A Digital Temperature Control System, B-VT-2000, with a dewar insert holder uses liquid nitrogen as a coolant for EPR spectra recorded at 122 K.

The (^1H and $^{13}C\{^1H\}$) NMR spectra from the polymers in $CDCl_3$ were recorded at 25.0 ± 0.1 °C using a Bruker AVANCE III 400 spectrometer. For NMR measurements, the isolated polymers were reprecipitated with methanol from $CHCl_3$ solutions, and then dissolved in $CDCl_3$.

SEC (Size Exclusion Chromatography) analyses were conducted using a Shimadzu Prominence LC system equipped with a LC-20AD pump, a DGU-20A5 degasser, a CBM-20A communication module, a CTO-20A oven and a RID-10A detector, connected to three PL gel columns (5 μm MIXED-C: 30 cm, Ø = 7.5 mm). Retention time was calibrated with standard monodispersed polystyrene using HPLC-grade $CHCl_3$ as eluent. PDI is M_w/M_n.

The films for DMA measurements were prepared in Teflon molds (disks of 65 mm) *via* solution-cast from saturated $CHCl_3$ solutions. The storage modulus (*E′*) and loss tangent (tan *δ*) were recorded as a function of temperature using a Netzsch Instruments DMA 242C, with a heating rate of 3.0 °C min^{-1}, working in the tensile mode at a fixed frequency of 1 Hz. Liquid N_2 was used to cool the sample and provide inert atmosphere for the analyses.

Results and discussion

ROMP of NBE and NBD

The five-coordinate complex $[RuCl_3(PCy_3)_2]$ (**1**) showed activity for ROMP of NBE at 25 °C, in the presence of EDA as carbene source, with fast gelation of the solution. Polymerizations were rapid and highly exothermic with the reaction being completed in less than 1 min. Fig. 1 shows the dependence of polyNBE yields on EDA concentration. The yield decreases with [EDA]/[Ru] molar ratio higher than 30 units, probably due to competition with the monomer for coordination onto the initiator active sites. The M_n values were not affected in the studied concentrations (Fig. 1), with PDI ranging from 1.4 to 2.0. The [EDA]/[Ru] molar ratio of 48 showed the lowest PDI value.

With [EDA]/[Ru] molar ratio of 48, the polyNBE yields decreased from 77 to 41 % when increasing the [NBE]/[Ru] molar ratio from 1,000 to 5,000, respectively (Fig. 2). The decrease in the yield is associated with a very fast gelation of the solution as the NBE feed increased, which probably blocked the access of more monomers into the Ru active center, avoiding the growing of the polymer chain. This can be associated with the reactivity of the initiator complex where more polymer chains are initiated, resulting in lower PDI values with M_n values in the same order of magnitude (10^5); PDI values decreased from 2.37 to 1.42 (Fig. 2). With [NBE]/[Ru] = 10,000, gelation occurred even more quickly, decreasing the yield even more (Fig. 2). Higher PDI values can be associated with disequilibrium in the initiation and propagation steps (as k_p/k_i ratio) owing to fast reactivity of the metal active species in a medium with higher monomer concentration. In contrast, rapid reaction start and low PDI value for

[NBE]/[Ru] = 5,000 are a clear evidence of the successful use of this complex, considering that the similar complex [$RuCl_2(=CHPh)(PCy_3)_2$] presented broad PDI.[14]

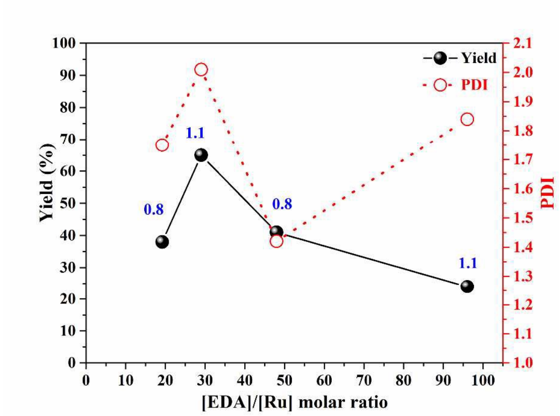


Fig. 1. Dependence of yield (●) on the [EDA]/[Ru] molar ratio for ROMP of NBE; [NBE]/[Ru] = 5,000 with 1.1 μmol of **1** in CHCl3 for 5 min at 25 °C. The inserted numbers are the M_n values in 10^5 g mol^{-1}.

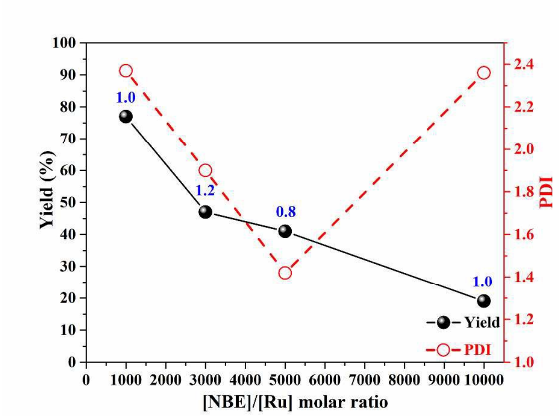


Fig. 2. Dependence of yield (●) and PDI (○) on the [NBE]/[Ru] molar ratio for ROMP of NBE; [EDA]/[Ru] = 48 with 1.1 μmol of **1** in $CHCl_3$ for 5 min at 25 °C. The inserted numbers are the M_n values in 10^5 g mol^{-1}.

The polyNBE yield increased with reaction time at 25 °C (Fig. 3). The increase was higher when similar experiments were conducted at 50 °C. This was expected because a greater number of monomers could access the active metal center to increase the polymer chain or to start a new polymer chain, mainly at 50 °C when the solution becomes less gelled. At 50 °C, a semi-quantitative yield was obtained for 60 min, whereas only *ca.* 60% of polyNBE was obtained at 25 °C for the same period of time. Different growing chains result as determined by increasing PDI values at higher temperatures. Further, the PDI values increased more intensely for long periods of reaction; this could be associated with the occurrence of secondary reactions, considering a very reactive propagating metal complex.[6, 11] When studying amine-phosphine Ru-based complexes,[25, 26] the solutions did not become gelled so rapidly, and higher temperatures favored both the induction period and the initiation step by releasing phosphine ligands to result in similar growing chains with M_n in the order of magnitude of 10^5 - 10^6. Under these conditions, the PDI values were more intensely affected with **1** than when using the amine-phosphine Ru-based complexes.[25-27, 29, 30]

Quantitative yields for ROMP of NBD were obtained at 25°C for 5 min in different [NBD]/[Ru] molar ratios (1,000; 3,000; 5,000), with immediate gelation of the solution and highly exothermic reaction. These features are consistent with a very reactive species which provides rapid induction, initiation and propagation reaction steps.[6, 11] The polymers were insoluble in $CHCl_3$ owing to the polyNBD-type network, which was expected to be cross-linked.[42]

High activity for ROMP of NBD agreed with the higher ring strain for NBD compared with NBE. Although thermodynamically favored, this was not observed when using the previous [$RuCl_2(PPh_3)_2(amine)_x$] type complexes that were more active for ROMP of NBE.[25-27, 29, 30] NMR studies revealed, in those cases, that NBD coordinated to the Ru^{II} center through the two double bonds of the bicycle.[28] A double coordination could represent a problem over the entire reaction (initiation and propagation, retarding the formation of metallocyclobutane intermediate), also there is possible competition in the formation of metal-carbene species in the induction period. However, the steric hindrance provided by PCy_3 most likely avoids the double coordination occurrence in the present case, resulting in good reactivity with NBD and 100% yield. In the case of Ru-amine-PPh_3 type complexes, recent calculus have suggested a phosphine-free active species, which could be more capable to undergo a double coordination from NBD because of the absence of steric hindrance around the metal coordination sphere.[43] Thus the phosphine-free metal complex would be less reactive. In addition, the strong σ-electron donation from the PCy_3 ligand favored the reaction with a more electron-deficient olefin to form polyNBD in a superior rate.

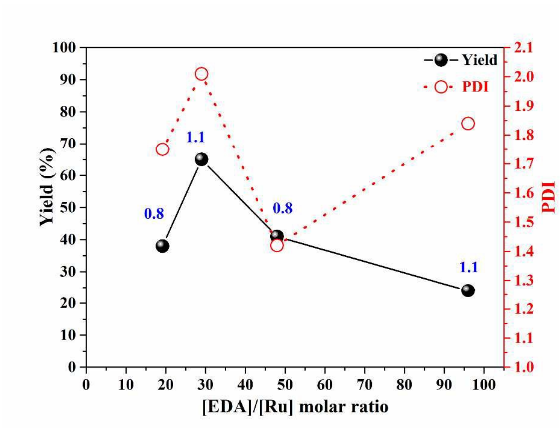
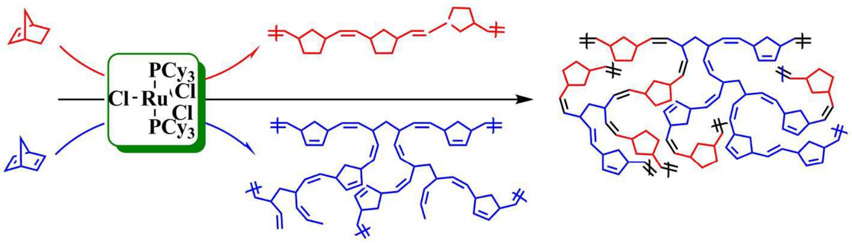


Fig. 3. Dependence of yield (●) and PDI (○) on reaction time for ROMP of NBE; [NBE]/[Ru] = 5,000 and [EDA]/[Ru] = 48 with 1.1 μmol of **1** in $CHCl_3$ at 25 (solid line) and 50 °C (dash line).

The different yields from ROMP of NBE and NBD with **1** under similar conditions can be associated with the type of polymer chain structure that is growing in each case (Scheme 2). In the case of NBD, the second olefin ring in polyNBD can open, even via vinyl addition.[44, 45] Thus more NBD monomers will be consumed before the solution becomes gelled.

It is possible to affirm that complex **1** is much more efficient for ROMP of NBD compared with [$RuCl_2$(=CHPh)(PCy_3)$_2$], which is reported as an efficient catalyst for ROMP of low strained cyclic olefins, although its molecular weight distributions are often a bit broader.[14, 16, 46, 47] Therefore, *in situ* formation of the metal-carbene species from **1** with EDA did not interfere in the complex activity in ROMP reactions, where perhaps the active species is similar to that from [$RuCl_2$(=CHPh)(PCy_3)$_2$].



Scheme 2. Illustration of homopolymerizations and copolymerization of NBE and NBD *via* ROMP.

Copolymerization of NBE and NBD

Copolymerization reactions between fixed amounts of NBE and different loads of NBD ([NBE]$_{5000}$[NBD]$_n$, with n = 500, 1500, and 3000) resulted in yields in the range of 42 - 61% (Table 1; Scheme 2), following the [NBD] increasing when the starting complex produced more polyNBD than polyNBE in the homopolymerizations. The materials were soluble in $CHCl_3$ and the data from SEC showed broad chains with low molecular weight, with a tendency to increase the PDI when increasing the [NBD] loads (Table 1). This draws attention to cross-liked chain type occurrence.

Table 1 Copolymer data obtained from different starting $[NBE]_{5000}[NBD]_n$ compositions (180 min; 25 °C). Fractions of cis double bonds and M_2/M_1 ratios were from NMR spectra (^{13}C; ^1H).

n value	Yield (%)	$M_n{}^a$ (10^3 g mol^{-1})	PDI	M_2/M_1 ratio^a Found / Calcd	$\sigma_c{}^{1,4}$ ^{13}C	$\sigma_c{}^{1,4}$ ^1H	$\sigma_c{}^{1',4'}$ ^{13}C	$\sigma_c{}^{1',4'}$ ^1H	$r_c.r_t$ $C^{1,4}$	T_g (°C)
500	42	24	2.87	0.08 / 0.10 (80%^{b})	0.42	0.43	0.53	0.54	1.14	82.4
1500	55	13	2.92	0.25 / 0.30 (83%^{b})	0.42	0.44	0.50	0.53	1.09	85.6
3000	61	6	3.33	0.55 / 0.60 (92%^{b})	0.42	0.41	0.52	0.54	1.00	90.0

[a] M_1 = NBE; M_2 = NBD

[b] (Found/Calcd) x 100

The ^{13}C NMR spectra of the isolated materials showed peaks in the range of 132-135 ppm, which are typical of olefinic carbon (Fig. 4). The NMR assignments confirmed the formation of poly[NBE-*co*-NBD], characterized by M_1M_2 and M_2M_1 heterodyads signals, in addition to homodyads (M_1M_1 and M_2M_2) signals, as described in the literature.[48, 49] The symbols M_1 and M_2 correspond to the NBE and NBD mer-units, respectively. The multiplet group centered at 134.85 ($C^{5',6'}$) was attributed to the M_2M_2 homodyads of non-opened NBD second double bond. The peaks at 133.93 and 133.03 ppm ($C^{2,3}$) were attributed to the M_1M_2 heterodyads and M_1M_1 homodyads, respectively. The peaks at 132.87 and 132.30 ppm ($C^{2',3'}$) were attributed to the M_2M_2 and M_2M_1 heterodyads, respectively.

Measurements of M_2/M_1 heterodyads ratios from ^{13}C NMR spectra indicated that 80-92% of the loaded NBD was inserted in the polymer backbone, which is in agreement with the higher yields of NBD (Table 1). Therefore, high NBD insertions and, consequently, higher yields were obtained when increasing the NBD amount in the starting composition. With the Ru^{II}-piperidine or Ru^{II}-(2,4-dimethyl-piperidine) complexes, 50% of NBD insertion was obtained in either case at the most.[27]

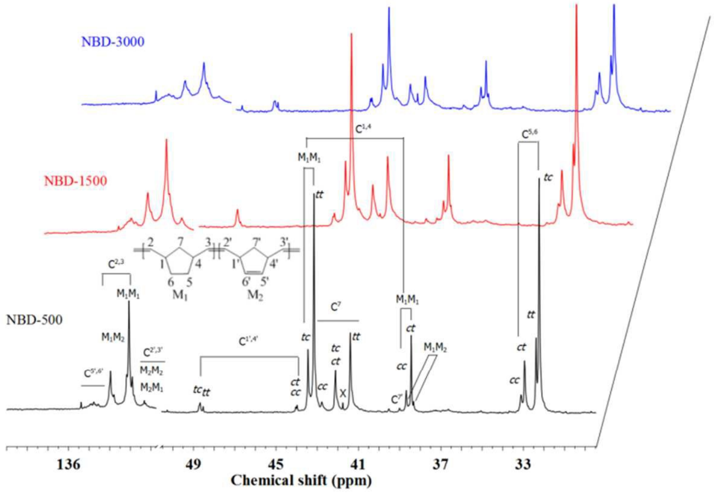


Fig. 4. ^{13}C-NMR spectra of poly[NBE-*co*-NBD] obtained from different starting $[NBE]_{5000}[NBD]_n$ compositions.

The reactivity ratios r_c (cc/ct) and r_t (tt/tc) for NBE units were in the range of 0.43-0.64 for r_c and 1.40-2.66 for r_t, giving an $r_c.r_t$ value of 1.00-1.14 (Table 1). The fraction of cis-double bonds (σ_c) was 0.42. The σ_c and $r_c.r_t$ values thus characterize a slightly trans polymer with a blocky distribution of cis and trans structures, considering that polymers with σ_c = 0.35–0.85 show blocky distribution ($r_c.r_t > 1$).[11, 50] The $r_c.r_t$ values for NBD units were not calculated because the signals for the M_2M_2 homodyads are not well split. The σ_c values determined from the δ_H in the ^1H NMR spectra at 2.41 and 2.77 ppm ($HC^{1,4}$; *trans*- and *cis*-NBE units, respectively) and at 3.18 and 3.54 ppm ($HC^{1',4'}$; *trans*- and *cis*-NBD units, respectively) are compatible with those obtained from the ^{13}C NMR spectra (Table 1).

From the DMA analyses at low temperatures, the storage modulus (E') curves showed that all copolymers were in the glassy state at the beginning of the measurement (Fig. 5). At temperatures ranging from 25 to100 °C, the storage modulus dropped in each case, reaching the rubbery plateau (Fig. 5). The difference between the E' values from each composition can be associated with the higher cross-linking degree for $[NBE]_{5000}[NBD]_{3000}$. The copolymers presented T_g values of 82.4, 85.6, and 90.0 °C and tan δ = 0.40, 0.42, and 0.45 for NBD loads with n = 500, 1500, and 3000, respectively (Fig. 6). These data represent an improvement in the T_g values, as the polyNBE presents T_g of *ca.* 37 °C.[27, 51] A small change in the Tg was observed as the NBD load increased (*ca.* 10 °C). PolyNBEs are amorphous and thermoplastic, with molecule chains chaotically arranged. Thus the increase in the T_g values results from the NBD presence in the copolymers, owing to the cross-linked structures.[27, 40, 41, 52]

The SEM micrographs for the sample with $[NBE]_{5000}[NBD]_{500}$ composition show a highly organized honeycomb-like pattern (Fig. 7). It was possible to obtain regular pores in the presence of a cross-linking agent, but the regularity on the copolymer morphology decreased as the NBD load increased more than the double, and this can be associated with the higher reactivity of **1** with NBD. Regularity decreased with increased tan δ values because the mobility of polymer chains was affected by the porosity organization and by the cross-linking degree when increasing the NBD loads.

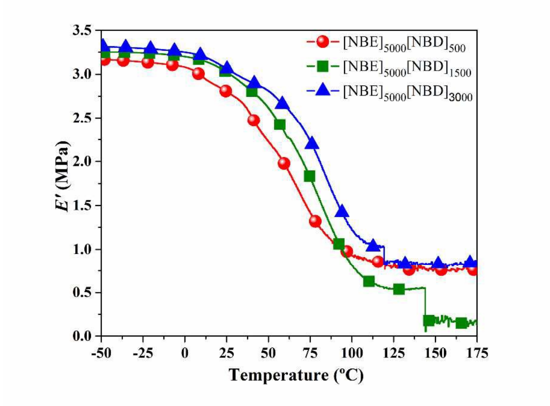


Fig. 5. Storage modulus curves for poly[NBE-*co*-NBD] obtained from different starting $[NBE]_{5000}[NBD]_n$ compositions.

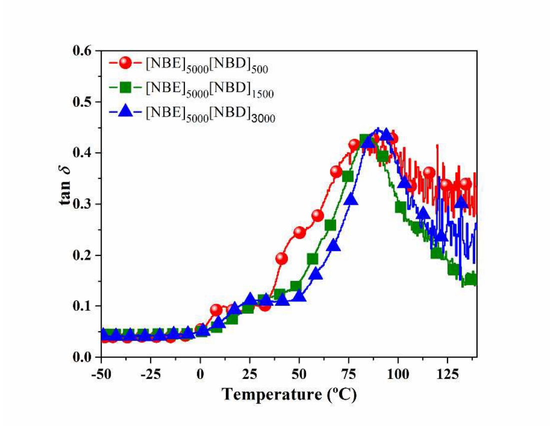


Fig. 6. Tan *δ* curves for poly[NBE-*co*-NBD] obtained from different starting $[NBE]_{5000}[NBD]_n$ compositions.

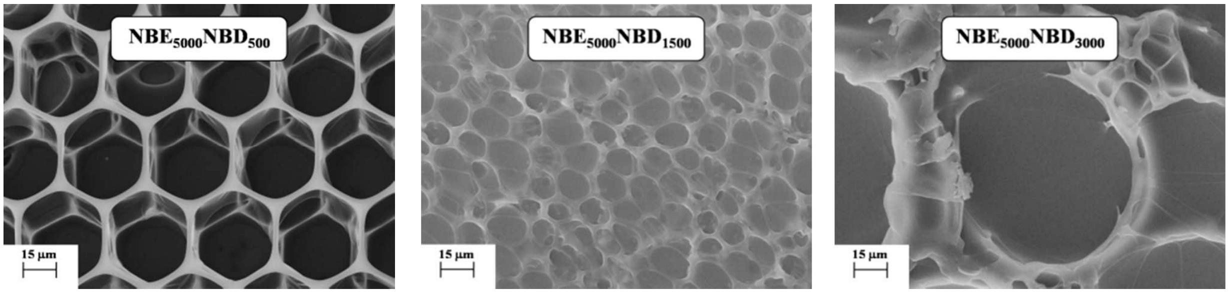


Fig. 7. SEM micrographs (3000x) for poly[NBE-*co*-NBD] obtained from different starting $[NBE]_{5000}[NBD]_n$ compositions.

EPR studies of [$RuCl_3(PCy_3)_2$]

The EPR spectrum of the paramagnetic [$RuCl_3(PCy_3)_2$] complex measured in the solid state (X band, 122 K) produced three signals. The *g* values are g_1 = 2.24, g_2 = 2.05, and g_3 = 1.89 (Fig. 8).[53, 54] Two hyperfine splitting signals were not defined due to the interaction with any other nuclei present in the complexes.[55] The five-coordinate complex showed three different axis, which is typical of a rhombic structure. In a solution of $CHCl_3$ with NBE and EDA, this complex shows a mixture of compounds (Fig. 9). The initial spectra shows several signals (g_1 = 2.27, g_2 = 2.05, and g_3 = 1.99), and a new signal is observed at *g* = 2.09 due to dissociation of the ligands and reaction with EDA to form the metal-carbene species (induction step), followed by coordination of NBE to start the ROMP reaction (initiation and propagation steps). After a few minutes, the signal at *g* = 2.27 disappears and the other signals are also consumed until a silence EPR spectrum is reached. The formation of a diamagnetic species can be associated with redox processes *via* a disproportionation reaction ($Ru^{III} \rightarrow Ru^{II} + Ru^{IV}$), but a high electronic density is required to obtain a high activity in ROMP reactions. Therefore, we believe that a main Ru^{II} complex is formed in the presence of NBE and EDA, following the EPR spectra. Another experiment was realized with ethyl vinyl ether(EVE) instead of NBE to eliminate the possibility of a polymer that can alter the viscosity of the medium, interfering in the solution homogeneity to record the spectrum. Similar EPR signal disappearance was observed after a few minutes.

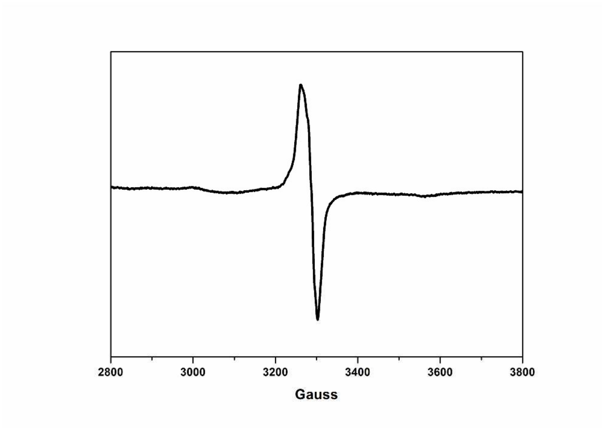


Fig. 8. EPR spectrum of [$RuCl_3(PCy_3)_2$] in solid state at 122 K.

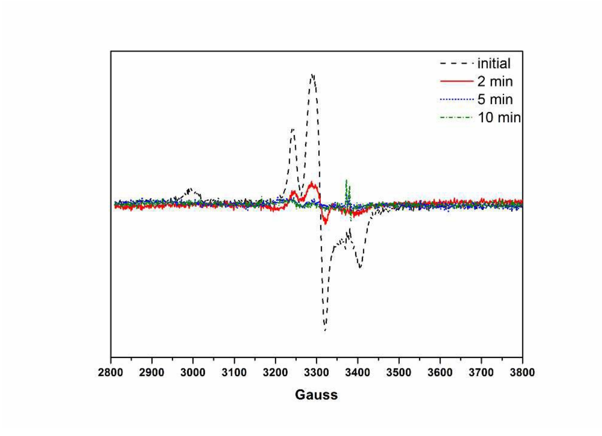


Fig. 9. EPR spectra of [$RuCl_3(PCy_3)_2$] in $CHCl_3$ in presence of NBE and EDA at 122 K.

Conclusions

A metal-carbene species generated *in situ* from the starting [$RuCl_3(PCy_3)_2$] (**1**) complex was able to polymerize very rapidly, *via* ROMP, strained cyclic olefins in non-degassed solution. Dependence of reactivity on reaction time and temperature was observed in the case of NBE, but quantitative yields of polyNBD were obtained regardless of time and temperature. In part, this difference can be associated with the type of polymer chain formed, where amorphous polyNBE and cross-linked polyNBD were obtained. The reactivity of the Ru species from **1** can be attributed to the σ-donor electronic effect and steric hindrance from the PCy_3 as ancillary ligand. The high electronic effect could cause instability in the metal center, allowing the formation of diamagnetic species, and the high steric hindrance could prevent the double coordination of NBD from occurring, as it does in the case of the others Ru-amine-based complexes. This could also justify the better reactivity with NBD compared with NBE. Hence, a high NBD content in poly[NBE-*co*-NBD] was obtained, resulting in cross-linked polymers with noticeable improvement in the T_g values when compared with polyNBE. The micrographs revealed that the morphological shapes of the copolymers were sensitive to NBD content, which can also be associated with the fast reaction with NBD. Complex **1** can produce a similar Grubbs first generation propagating species, except for the fact that the first metal-carbene species is prepared *in situ*.

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Table of contents

$[RuCl_3(PCy_3)_2]$ presented high activity for ROMP of norbornene and norbornadiene under air, in presence of ethyl diazoacetate, resulting in copolymers with high T_g values and organized morphologies